

# New ferromagnetic nitrides, CaN and SrN, and their synthesis process

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We introduce new type of ferromagnets, CaN and SrN, which were designed using first-principles calculations. These are half-metallic ferromagnets and they have magnetic moments of  $1 \mu_B$  per chemical formula unit. Out of the typical structures of binary compounds, the rock-salt structure is the most stable form for both CaN and SrN. The majority of the magnetic moment of these compound originates from the N sites since the  $p$  states of N are spin-polarized. Their formation energies were calculated and the results show that it should be feasible to synthesize these materials. The structural stability of CaN was confirmed by performing first-principles molecular dynamics simulations. We propose a synthesis process for CaN based on the first-principles.

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Synthesis of substances which do not exist in nature promises to have an enormous potential to produce materials having excellent properties. Recent experimental reports of the syntheses of PtN,[1] IrN, IrN<sub>2</sub> and OsN<sub>2</sub>[2] demonstrate that it is possible to synthesize new materials using special experimental techniques.

On the other hand, the reliability of standard first-principles calculations has been widely recognized. They are very powerful tools for predicting the physical and chemical properties of materials including the individual characteristics of elements based on their electronic configurations. In particular, structural properties and physical quantities calculated from them highly accurate are in good agreement with experimentally measured values. To date there has been no example of an incorrect prediction of the magnetic properties of simple transition metals compounds using a spin-dependent generalized gradient approximation (spin-GGA) for an exchange-correlation functional. These facts imply that it is possible to obtain accurate predictions of structural and magnetic properties without performing experiments. This allows us to design new materials before they are synthesized in the laboratory. Our aim is to design new materials and discover the synthesis processes of these new materials using theoretical techniques.

In this study, we focus on nitride compounds. It is well known that nitrides prefer the ferromagnetic state. For example, most rare earth nitrides become ferromagnetic[3] and usually crystallize in a rock-salt(RS) structure. These facts encourage us to consider replacing the rare earth elements with Ca and Sr since their ionic radii are close to those of the rare earth ions, and from our previous results we confirmed that Ca- and Sr-pnictides are ferromagnetic[4]. Such replacement is natural in view of the Zintl phase[5]. There is thought to a probability of being able to synthesize RS-CaN and RS-SrN if appropriate experimental techniques are employed. In fact, PtN has been synthesized in a high pressure environment[1].

Many predictions have been made[6, 7, 8, 9] based on density functional theory (DFT)[10] using the local spin density approximation (LSDA) or the spin-

GGA, and these predictions have been experimentally confirmed.[11, 12, 13, 14, 15, 16] Spin-GGA calculations of the electronic structures and the magnetic properties of materials which consist of atoms which have only  $s$  and  $p$  electrons tend to be the most reliable, and those of second-row elements such as carbon and oxygen, give satisfactory results.

We performed first-principles calculations based on DFT using the LSDA or the spin-GGA for RS-CaN and RS-SrN. Typical DFT codes were used to confirm our results [17, 18, 19]. The total energies of some structures and each magnetic state and detailed electronic structures (e.g. densities of states (DOS) and magnetic moments) were calculated by the APW+lo method.[17] The value of  $R_{MT}K_{max}$  was fixed at 8.00, where  $R_{MT}$  is the minimum muffin-tin (MT) radius and  $K_{max}$  is the maximum reciprocal lattice vector. The MT radii of Ca and Sr ( $MT_{Ca(Sr)}$ ) are  $0.22a$ ,  $0.27a$  and  $0.45a$  for the zinc-blende(ZB), RS, and CsCl structures, respectively, where  $a$  is the lattice constant. The MT radii of N ( $MT_N$ ) are  $0.18a$ ,  $0.221a$ , and  $0.3681a$  for the ZB, RS, and CsCl structures, respectively. For the wurtzite structure  $MT_{Ca(Sr)}$  and  $MT_N$  were set to fixed values for each volume and ratio between  $MT_{Ca(Sr)}$  and  $MT_N$  is 1.3:1 and the sum of both MT radii is about 95% of atomic distances. We used an angular momentum expansion up to  $l_{max} = 10$ . The energy convergence criterion was set to 0.001 mRy. Twenty k-points were taken in the irreducible Brillouin zone. To confirm magnetism in the four types of structures, we performed more accurate calculations which employed ten times larger k-point sampling in the irreducible zone. By doing this we were able to confirm the definite existence of magnetism for these cases. To check the magnetism, we performed calculations for RS-CaN using the KKR-CPA-LDA method [18]. For Moruzzi-Janak-Williams method was used to calculate the exchange-correlation functional [20]. For this calculation we used an angular momentum expansion up to  $l_{max} = 2$ . We used the Espresso-code[19] to perform first-principles molecular dynamics simulations and also to check the magnetism of RS-CaN. The energy cut-off

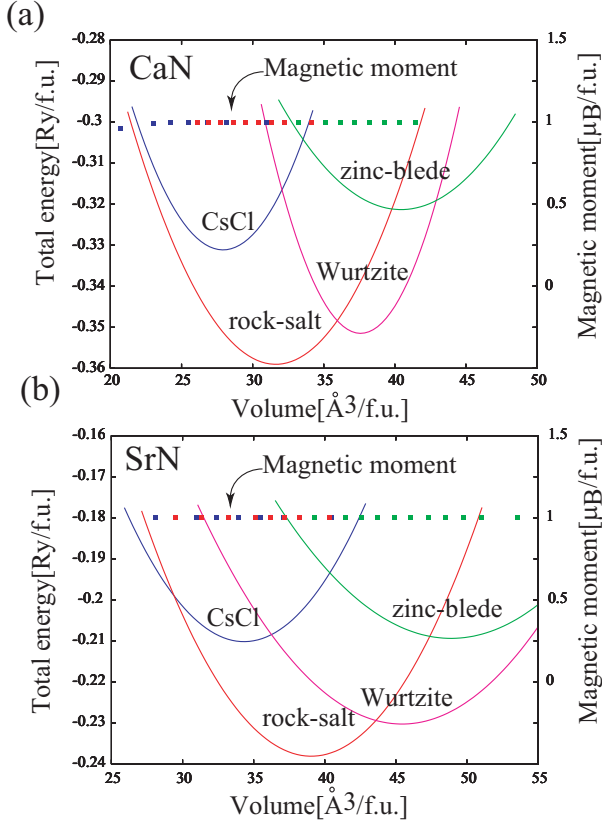


FIG. 1: (Color online) Total energies and magnetic moments of (a) CaN and (b) SrN are plotted as a function of volume. The magnetic moment per chemical formula unit is shown on the right vertical axis.

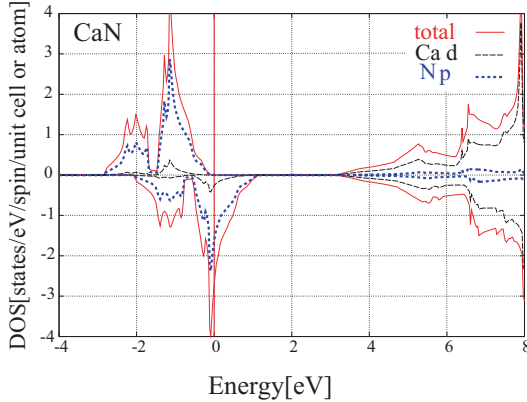


FIG. 2: (Color online) The DOSs of RS-CaN. The partial DOS is defined in the muffin-tin sphere used in the band calculations.

of plane waves was 80 Ry.  $8 \times 8 \times 8$  k-point meshes were used for first Brillouin zone integration. Other details concerning the calculations are described later.

In Figs. 1(a) and 1(b), the total energies of CaN and SrN are plotted as a function of volume per chemical formula unit. We chose the RS structure along with the

TABLE I: The magnetic moment of CaN. In units of  $\mu_B$ .

structure	RS	ZB	CsCl
Toatl	1.000	1.000	1.000
Ca	0.038	0.038	0.033
N	0.794	0.787	0.822
Interstitail	0.168	0.175	0.145

other typical structures of binary compounds, namely, ZB, wurtzite and CsCl structures. The most lowest structure is the RS structure, while the wurtzite structure is the second lowest stable structure. The wurtzite structure was optimized with respect to both  $c/a$  and the internal parameter. We checked the stabilities against tetragonal distortion for the RS, ZB and CsCl structures and confirmed that the RS and the CsCl structures are stable. In particular, the stability of the cubic structure for the RS structure is doubly confirmed on the basis of these total energy calculations and the first-principles molecular dynamics simulations described below. By contrast, tetragonal distortion reduces the total energy of the ZB structure, which is similar to the case of CaAs in the ZB structure[4]. In the ZB structure with tetragonal distortion,  $c/a=1.0$  is the maximum energy point and  $c/a=0.6$  is the minimum energy point. The energy difference between these two points is about 0.53eV(0.039Ry) for CaN and 0.23eV (0.017Ry)for SrN. Based on these differences, the distorted ZB structure is thought to have almost the same energy as the wurtzite one (Figs. 1(a),(b)).

The four structures used in the calculations for CaN and SrN are of half-metal as well as ferromagnetic in spite of not containing any transition or rare earth metals. In other words, CaN and SrN are ferromagnetic without having any  $d$  or  $f$  electrons. The magnetic moments are plotted in Figs. 1(a) and (b). The calculated magnetic moments for both CaN and SrN are  $1 \mu_B$ , which is evidence of their half-metallicity. The DOSs of RS-CaN are shown in Fig. 2. The total DOS indicates completely spin-polarized electronic states at the Fermi level. In the other structures, CaN and SrN are also half-metallic as shown in Fig. 1, while the magnetic moments of Ca(P,As,Sb) and Sr(P,As,Sb) depend on the structures and lattice constants or volumes.[4] The partial DOSs indicate that the principal component at the Fermi level consists of  $p$  states of N. As expected, the majority of the magnetic moment resides on the N atom as shown by Table I. The magnetic moment at the Ca or Sr sites is quite small being less than that of the interstitial region.

We show in Fig. 3 the difference in the total energies for the ferromagnetic, antiferromagnetic and non-magnetic states for RS-CaN. The energy difference between the ferromagnetic and antiferromagnetic states for RS-CaN is more than 0.1 eV. These values are quite large.

We further confirmed the structural stability of CaN having the RS structure by using first-principles molecular dynamics simulations. The simulations were per-

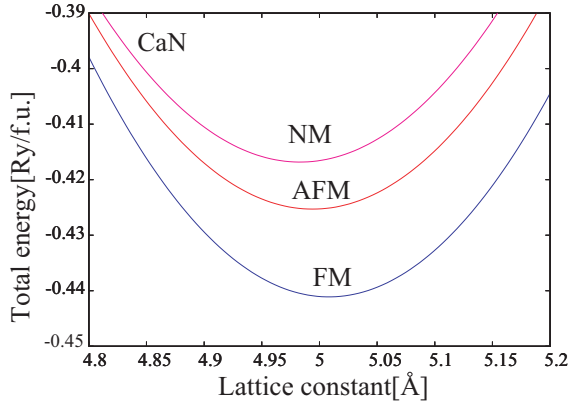


FIG. 3: (Color online) Total energies as a function of the lattice constant are compared for the ferromagnetic (FM), antiferromagnetic (AFM) and nonmagnetic (NM) states of CaN, where RS structure is assumed for both substances.

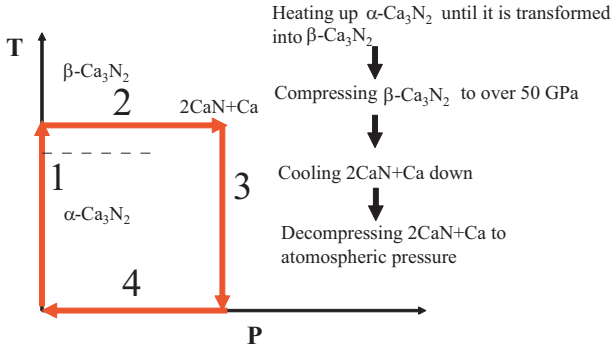


FIG. 4: (Color online) A promising synthesis process for CaN.

formed using the cubic unit cell, which contains eight atoms and is four times larger than the primitive cell, as the starting cell. We did not assume any symmetry for the atomic positions, that is, we employed a triclinic structure. We performed two types of molecular dynamics simulations; (1) a first-principles damped dynamics simulation using a variable cell, and (2) a first-principles constant-pressure and temperature molecular dynamics simulation using the Parrinello-Rahman method, where we used the velocity scaling method to control the temperature. The purpose of simulation (1) was to confirm whether the RS structure is at least metastable with respect to changes in the internal atomic positions and in the shape of the unit cell, while the purpose of simulation (2) was to confirm the stability of the RS structure at finite temperature and atmospheric pressure. From simulation (1) we confirmed that atomic forces become negligibly small (less than  $1.0 \times 10^{-4}$  Ry/a.u.) and that atomic positions in the RS structure are at least metastable. From simulation (2) we confirmed that the RS structure is stable at atmospheric pressure and finite temperatures (130 K, 210 K, and 760 K). These results support the possibility that CaN having the RS structure

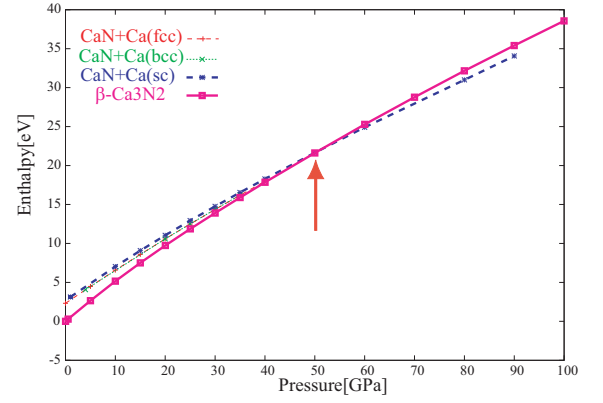


FIG. 5: (Color online) The enthalpy of  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> and the sum, 2CaN+Ca, as a function of pressure. Three types of structure of Ca are assumed and plotted.

would be stable if it can be synthesized.

We estimated the formation energy defined by  $E_{\text{formation}} = E_{\text{tot}} - (E_{\text{Ca(Sr)}} + E_{\text{N}_2}/2)$  for the RS, ZB and CsCl structures.  $E_{\text{Ca(Sr)}}$  is the total energy of the bulk Ca (Sr) per atom at a atmospheric pressure which we evaluated using the fcc structure.  $E_{\text{N}_2}$  denotes the total energy of an isolated N<sub>2</sub> molecule. The energy of the molecule is calculated using a large unit cell ( $a=18$  Å, for an fcc cell containing one molecule). The calculated formation energies are -11.2 eV(RS), -10.7 eV(ZB), and -10.8 eV(CsCl) for CaN, and -10.8 eV(RS), -10.5 eV(ZB), and -10.5 eV(CsCl) for SrN, respectively. These results suggest that CaN and SrN having the three structures investigated, will not decompose once they have been formed. Out of these structures, the formation energy of the RS is lower than that of the other structures for both CaN and SrN.

Under normal conditions, Ca and N usually form Ca<sub>3</sub>N<sub>2</sub> in the  $Ia\bar{3}(\alpha\text{-Ca}_3\text{N}_2)$  structure. This structure is transformed to  $\beta\text{-Ca}_3\text{N}_2$  whose structure is  $P\bar{3}m1$ [21] when the temperature is increased. We compared the formation energies of RS-CaN with that of Ca<sub>3</sub>N<sub>2</sub> for both  $\alpha$ - and  $\beta$ -Ca<sub>3</sub>N<sub>2</sub>. The formation energy of the  $\alpha$  phase is about 2.9 eV lower than that of 2 CaN + Ca. The formation energy of the  $\beta$  phase, however, is about 2.5 eV higher than that of 2 CaN + Ca. This fact implies that if CaN is formed using an appropriate method, it may be more stable than  $\beta\text{-Ca}_3\text{N}_2$ .

We now proceed to propose ideas for how CaN and SrN can be synthesized in the laboratory. In this paper, we only consider RS-CaN. Based on the above results, several possible methods and processes suggest themselves. One of them is high pressure and high temperature synthesis. We propose the synthesis process based on first-principles calculations. A scenario for synthesizing RS-CaN is illustrated in Fig. 4. Firstly, heat  $\alpha\text{-Ca}_3\text{N}_2$  until it is transformed into  $\beta\text{-Ca}_3\text{N}_2$  whose structure is  $P\bar{3}m1$ [21] and then compress it using a pressure higher than 50 GPa until the reaction  $\beta\text{-Ca}_3\text{N}_2 \rightarrow 2\text{CaN} + \text{Ca}$  occurs. After

that, cool the product and decompress it to atmospheric pressure. In order to evaluate the transition pressure, we give the enthalpy differences in Fig. 5, where we show the enthalpy of  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> and that of the sum of the two phases, 2CaN+Ca. We assumed the structures of Ca as fcc, bcc, or sc. As the pressure is increased, the structure of Ca is transformed from the fcc into bcc (at 20 GPa) into sc (at 32 GPa). The enthalpy of 2CaN+Ca (sc) becomes lower than that of  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> at about 50 GPa. Based on the calculations of the formation energy of RS-CaN and the constant pressure and temperature first-principles molecular dynamics simulation, 2CaN+Ca(sc) should not decompose once it has been formed. This result strongly suggests that  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> is transformed into RS-CaN with sc Ca. The transition temperature from  $\alpha$ -Ca<sub>3</sub>N<sub>2</sub> to the  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> is only represented by a dashed line, since it has not been precisely determined experimentally. Based on this scheme, laser heating may heat the sample to a temperature that is too high for the  $\beta$ -phase. Accurate experimental determination of the phase diagram of Ca<sub>3</sub>N<sub>2</sub> is required to determine the transition temperatures.

In the view of experiment, we might consider  $\beta$ -Ca<sub>3</sub>N<sub>2</sub> + N<sub>2</sub>  $\rightarrow$  6 CaN reaction. In this process N<sub>2</sub> is liquid and is used to compress hydrostatically. We have not checked the influence of pressure for that process yet, and we do not deny the possibility.

The other method having a high probability of success is molecular beam epitaxy. To synthesize the RS structure, we propose a synthesis process using a superlattice structure, similar to the fabrication process of CrAs/GaAs which used a superlattice structure[11]. On surfaces, processes may occur which are very different from those that occur in the bulk material and, conse-

quently structures that are different from those in the bulk may be produced. This is the case of ZB-CrAs, which is unstable according to total energy calculations. We do not deny the existence of other synthesis processes, for example, heating to a liquid state and then compressing to an appropriate pressure, similar to the process for synthesizing PtN. Our suggestions are only two of several possible processes. We hope that our suggestion inspires experimentalists to synthesize CaN and SrN.

In conclusion, we have designed and investigated new ferromagnetic nitrides, CaN and SrN. These are half-metallic ferromagnets as a result of the polarization of  $p$ -orbitals of N. The process for synthesizing RS-CaN using a high pressure is proposed based on the results of the first-principles calculations. The development of experimental techniques may allow us to synthesize such new materials.

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- [1] E. Gregoryanz, C. Sanloup, M. Somayazulu, J. Badro, G. Fiquet, H. K. Mao, and R. J. Hemley, *Nature Mater.* **3**, 294 (2004).
  - [2] J. C. Crowhurst, A. F. Goncharov, B. Sadigh, C. L. Evans, P. G. Morral, J. L. Ferreira, and A. J. Nelson, *Science* **311**, 1275 (2006).
  - [3] K. A. Cshneidner and L. Eyring, *Handbook on the Physics and Chemistry of Rare Earths Vol. 1 Metals* (Amsterdam: North-Holland) p. 532 (1978).
  - [4] M. Geshi, K. Kusakabe, H. Tsukamoto, and N. Suzuki, *The American Institute of Physics (AIP), ICPS-27 proceedings* **772**, 327 (2005).
  - [5] K. Kusakabe, T. Ogitsu, and S. Tsuneyuki, *J. Phys. Condens. Matter* **10**, 11561 (1998).
  - [6] M. Shirai, *Physica E* **10**, 143 (2001).
  - [7] K. Sato and H. Katayama-Yoshida, *Jpn. J. Appl. Phys.* **40**, L485 (2001).
  - [8] K. H. Schwarz, *J. Phys. F: Met. Phys.* **16**, L211 (1986).
  - [9] I. I. Mazin, *Appl. Phys. Lett.* **77**, 3000 (2000).
  - [10] P. Hohenberg and W. Kohn, *Phys. Rev.* **136**, B864 (1964).
  - [11] H. Akinaga, T. Manago, and M. Shirai, *Jpn. J. Appl. Phys.* **39**, L1118 (2000).
  - [12] G. T. Thaler, M. E. Overberg, B. Gila, R. Frazier, C. R. Abemalhy, S. J. Peaton, J. S. Lee, S. Y. Lee, Y. D. Park, G. Khim, et al., *Appl. Phys. Lett.* **80**, 3964 (2002).
  - [13] T. Sasaki, S. Sonoda, Y. Yamamoto, K. Suga, S. Simizu, K. Kindo, and H. Hori, *J. Appl. Phys.* **91**, 7911 (2002).
  - [14] K. P. Kämper, W. Schmitt, G. Güntherodt, R. J. Gambino, and R. Ruf, *Phys. Rev. Lett.* **59**, 2788 (1987).
  - [15] R. J. S. Jr., J. M. Byers, M. S. Osofsky, B. Nadgorny, T. Ambrose, S. F. Cheng, P. R. Broussard, C. T. Tanaka, J. Nowak, J. S. Moodera, et al., *Science* **282**, 85 (1998).
  - [16] S. F. Cheng, G. T. Woods, K. Bussmann, I. I. Mazin, R. J. S. Jr., E. E. Carpenter, B. N. Das, and P. Lubitz, *J. Appl. Phys.* **93**, 6847 (2003).
  - [17] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave + Local Orbitals Program for Calculating Crystal Properties* (Karlheinz Schwarz, Techn. Universität Wien, Austria) (2001).
  - [18] H. Akai, *J. Phys. Soc. Jpn.* **51**, 486 (1982).
  - [19] S. Baroni, A. D. Corso, S. de Gironcoli, P. Giannozzi, C. Cavazzoni, G. Ballabio, S. Scandolo, G. Chiarotti,

- P. Focher, A. Pasquarello, et al., <http://www.pwscf.org/>.
- [20] V. L. Moruzzi, J. F. Janak, and A. R. Williams, *Calculated Electronic properties of Metals*(Pergamon, New York, pp.11) (1978).
- [21] P. Willars, *Pearson's Handbook* vol. 1 p. 1080 (1997).